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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US92/10291 <b>(22) International Filing Date:</b> 30 November 1992 (30.11.92)  <b>(30) Priority data:</b> 801,199 2 December 1991 (02.12.91) US  <b>(71) Applicant:</b> ALLIED-SIGNAL, INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).  <b>(72) Inventors:</b> NALEWAJEK, David ; 22 Cedar Court, West Seneca, NY 14224 (US). BASU, Rajat, Subhra ; 167 Shetland Drive, Williamsville, NY 14221 (US). WILSON, David, Paul ; 118 Waxwing Court, East Amherst, NY 14051 (US). VAN DER PUJ, Michael ; 32 Joanne Lane, Cheektowaga, NY 14227 (US). SWAN, Ellen, Louise ; 4584 Dickersonville Road, Ransomville, NY 14131 (US). LOGSDON, Peter, Brian ; 1536 Kingston Avenue, North Tonawanda, NY 14120 (US). ZYHOWSKI, Gary, John ; 26 Running Brook Drive, Lancaster, NY 14086 (US). INGHAM, Hepburn ; 1153 South Lee Street, #206, Des Plaines, IL 60016 (US). HARNISH, Daniel, Franklin ; 77 Middlebury Road, Orchard Park, NY 14127 (US). RODGERS, Joel, Edward ; 2729 Pales Verdes Drive West, Pales Verdes Estates, CA 90274 (US).		<b>(74) Agent:</b> ROONEY, Gerard, P.; Allied-Signal Inc., Law Department (C.A. McNally), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).  <b>(81) Designated States:</b> AU, BB, BG, BR, CA, CS, DK, FI, HU, JP, KP, KR, LK, MG, MN, MW, NO, PL, RO, RU, SD, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

**(54) Title:** MULTIPLE SOLVENT CLEANING SYSTEM**(57) Abstract**

A non-aqueous cleaning process uses an organic solvent for removing soil or surface contamination from contaminated articles such as printed circuit boards which are cleaned by immersion into a sump compartment of a cleaning tank containing the organic cleaning solvent. The organic solvent is preferably a hydrocarbon solvent. The cleaned articles, now coated with the organic cleaning solvent, are then disposed in a rinsing sump containing a fluorocarbon based rinsing solvent having an affinity for the organic cleaning solvent. The organic solvent is thus removed from the articles which are then dried without waste water as in a conventional solvent vapor degreasing solvent process.

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MULTIPLE SOLVENT CLEANING SYSTEM

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Technical Field

The present invention relates to a method and apparatus of cleaning contaminated articles and apparatus therefore and, more particularly, to the defluxing or degreasing of parts in a non-aqueous cleaning system utilizing an organic solvent for cleaning the parts and a nonflammable fluorocarbon solvent.

15

Background Art

Solvent vapor phase degreasing and defluxing is a process of immersing a soiled substrate (e.g., a printed circuit board or a fabricated metal, glass, ceramic, plastic, or elastomer part or composite) into a boiling, nonflammable liquid such as a chlorocarbon or chlorofluorocarbon fluid or admixture, followed by rinsing the part in a second tank or cleaning zone by immersion or distillate spray with a clean solvent which is the same chlorocarbon or chlorofluorocarbon as used in the first cleaning zone. The parts are then dried by maintaining the cooled part in the condensing vapors until temperature has reached equilibrium.

30

Solvent cleaning of various types of parts generally occurs in batch, hoist-assisted batch, conveyor batch, or in-line type conveyor degreaser and defluxer equipment. Such in-line conveyor degreaser and defluxer equipment are disclosed in co-pending U.S. patent application Serial No. 07/410,216, filed September 21, 1989, (entitled Cold Air Lock Vapor

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Seal"), now U.S. Patent 5,007,179, commonly assigned to the assignee of the present invention. Parts may also be cleaned in open top defluxing or degreasing equipment, such as that disclosed in U.S. Patent  
5 Application Serial No. 07/587,893, filed September 25, 1990, also commonly assigned. In both types of equipment, the entrance and/or exit ends of the equipment are generally in open communication with both the ambient environment and the solvent within the  
10 equipment. In order to minimize the loss of solvent from the equipment by either convection or diffusion, a common practice in the art is to use water-cooled or refrigerant-cooled coils which create a condensed vapor blanket over a hot or ambient zone region in the  
15 degreaser/defluxer tank, such as disclosed in U.S. Patent 4,261,111 to Rand.

Therefore, in the foregoing solvent vapor phase degreasing process, it is generally known to use a  
20 single organic chlorocarbon or chlorofluorocarbon (CFC) fluid to perform the cleaning, rinsing, and drying steps. The use of CFC-113 and Freon type solvents have been, in the past, particularly popular. However, the vapor diffusion thereof into the environment has been  
25 implicated in recent scientific studies to be one of many possible contributing causes to the undesirable global depletion of stratospheric ozone, and the production and use of such chlorofluorocarbons is currently regulated and will be phased out in the U.S.  
30 by the end of this decade. In response to environmental concern, hydrochlorofluorocarbon (HCFC) based solvents have been developed in the last few years to provide more environmentally acceptable alternatives to CFC based vapor phase decreasing and defluxing processes.  
35 While these materials have been shown to be excellent

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CFC substitutes for a variety of cleaning applications, they are considered to be an interim replacement to CFCs since they still process a small, but finite, ozone depletion potential, although it is much lower than that of the CFCs they are replacing. Hence, these HCFC solvents are also proposed for global phase out in the near future. It is generally believed that organic solvents which do not contain chlorine, bromide, or iodine atoms will not contribute to stratospheric ozone depletion. However, organic chemicals which do not contain the above halogen atoms, such as hydrocarbons, alcohols, esters, ethers, ketones, etc., usually contain undesirable flammability or reactivity properties. Per fluorinated hydrocarbons and hydrofluorocarbons possess many desirable solvent properties: zero ozone depletion potential; stable, non-reactive, high compatibility with plastics; good water displacement potential; generally non-toxic and inert, and ideally suited to vapor phase solvent cleaning equipment. However, perfluorocarbons have been found to be very poor solvents for many common organic and inorganic soils, e.g., fluxes. Hydrofluorocarbons offer improved but still limited cleaning ability over perfluorocarbon as the amount of fluorine content on the molecule diminishes, but low fluorine-content hydrofluorocarbons may start to exhibit undesirable flammability properties comparable to their hydrocarbon analogs.

Other types of cleaning processes such as aqueous cleaning exist. Aqueous cleaning generally involves the cleaning of a substrate or a part in an aqueous solution of detergents or surfactants, followed by multiple rinsing steps with purified water. The part is then dried by



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lengthy evaporation in air or by energy intensive thermal drying machines. This process is not always desirable due to the high energy cost for drying and the additional capital investment and  
5 operating cost burden to provide aqueous waste water cleanup required by state and local authorities before sewerage to ground water.

Another cleaning process, semi-aqueous  
10 cleaning, consists of cleaning a substrate in a hydrocarbon solvent based on, for example, terpenes, esters, or petroleum distillates having a high affinity for oils, waxes, and greases being cleaned from the parts, with or without the  
15 aid of a surfactant. The cleaned substrate is rinsed of the high boiling hydrocarbon solvent with multiple rinsing steps using purified water. The hydrocarbon solvent is phase separated back to the wash sump while the aqueous effluent must  
20 be processed before sewerage to ground water. Consequently, high costs associated with drying energy and with processing waste effluent are evident, similar to the before mentioned aqueous cleaning process. A further drawback is that the  
25 hydrocarbon solvent usually possesses a flash point and this must be carefully handled or blanketed with a nonflammable compressed gas such as nitrogen to avoid explosion. Nitrogen gas is much more fugitive than the dense vapors of a  
30 fluorocarbon contained in a condensing zone. Furthermore, in a number of applications, while the substrate to be cleaned may be compatible with the hydrocarbon solvent, some plastics or metals may be incompatible with the aqueous rinse  
35 solvent, resulting in water absorption or rusting

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of the substrate.

Disclosure of the Invention

5       It is accordingly one object of the present invention to provide a non-aqueous cleaning system for degreasing or defluxing parts in an environmentally safe manner.

10       Another object of the invention is to provide a non-aqueous cleaning system which does not use water for rinsing, and there does not exist a necessity for aqueous waste water cleanup, and whereby said non aqueous cleaning  
15 system can be used in cases where materials are incompatible with water.

      Still a further object is to provide a non-aqueous cleaning system avoiding the need for  
20 drying by lengthy evaporation of rinsing fluid in air or by energy intensive thermal drying methods.

      Yet a further object is to provide a non-  
25 aqueous cleaning system utilizing an organic liquid cleaning agent for cleaning the parts and a rinsing agent having at least a slight volubility for the organic cleaner for rinsing the organic cleaner from the part and which  
30 rinsing agent is capable of drying from the part using small amounts of energy.

A non-aqueous cleaning process for removing residual soils or surface contamination from a  
35 part, in accordance with the present invention,

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comprises the steps of introducing the part into contact with an organic cleaning fluid of sufficient solvency to substantially remove said contamination and then removing the part from the organic fluid for rinsing in a rinsing agent having at least some degree of volubility for the organic cleaner to remove same from the substrate. The substrate is immersed in the rinsing agent, sprayed with the rinsing agents exposed to vapors of the rinsing agent, or any combination of the above. When removed from the vapor the part is essentially clean and dry.

Preferably, the non-aqueous cleaning system of this invention utilizes a two tank cleaning process wherein a first tank contains the organic solvent and a second tank contains the rinsing agent. The parts or substrates to be cleaned may be conveyed from the cleaning tank to the rinsing tank utilizing known conveyor or hoist means. The tanks may be part of conventional or known in-line conveyORIZED degreasing/defluxing equipment, separate open top defluxing tanks, or open top defluxing tanks modified to contain the cleaning and rinsing tanks or sumps.

In accordance with another feature of the invention, a non-aqueous cleaning process for removing residual soils or surface contamination from parts comprises the steps of introducing the substrate or part into an organic fluid of sufficient solvency to remove residual contamination from the parts. The parts are then rinsed by contact with a second organic solvent of lesser solvency for the soils or surface

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contamination than exhibited by the first organic fluid solvent but having excellent solvency characteristics towards the first solvent. The second solvent (rinsing agent) may be chosen preferably from the fluorocarbon class of solvents which contain at least one fluorine atom attached to an organic backbone comprised of two or more carbon atoms, with optionally other atoms also attached to the backbone such as oxygen, sulfur, nitrogen, phosphorous, hydrogen, or other halogen atoms; or less preferably the rinsing agent may be chosen from other classes of solvents such as alcohols, ethers, esters, ketones, hydrocarbons, and other non-aqueous media. The parts are then dried by holding under an inert vapor blanket which lessens or mitigates the flammability of the first organic cleaning solvent, or, if flammable, the second rinse solvent, where such flammability masking vapor blanket may be formed by at least one of nitrogen, carbon dioxide, perfluorocarbon, hydrofluorocarbon, or hydrochlorocarbon.

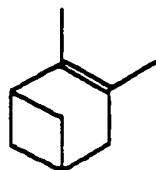
In one embodiment the cleaning can be done in a system where a solution of the hydrocarbon solvent and the fluorocarbon solvent is mixed together optionally with a surfactant as a solubilizing agent in a degreaser. The fluorocarbon, being more volatile, provides a flammability suppression blanket. The same fluorocarbon would be used in the adjacent rinse sump for an initial immersion or spray liquid rinse followed by a final rinse in the vapor.

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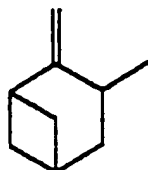
In the simplest embodiment, the cleaning can be done in a one sump system where a solution of the hydrocarbon solvent and the lower boiling fluorocarbon solvent is mixed together optionally with a surfactant as a solubilizing agent. The fluorocarbon, being more volatile, provides a flammability suppression blanket, and if the soiled part which has been immersed in the cleaning mixture is held in the condensing fluorocarbon vapors for a sufficiently long period of time, the part can be removed from the vapor phase clean and dry.

The organic cleaning solvent can be selected from linear or branched alkyl or alkanol monocarboxylic or dicarboxylic esters having at least one carbon atom in the ester moiety and such solvent most preferably having a flash point greater than 200°F, or less preferably having a flash point greater than 150°F. The organic fluid may also be selected from linear or cyclic hydrocarbons containing at least one olefinic bond endo or exo to the ring. The hydrocarbon cleaning agent may comprise pinene and/or camphene, or may comprise terpinene, limonene, terpinolene, terpineol, linalol, and other related members of the terpene family.

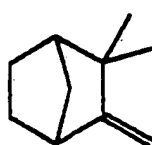
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ALPHA-PINENE

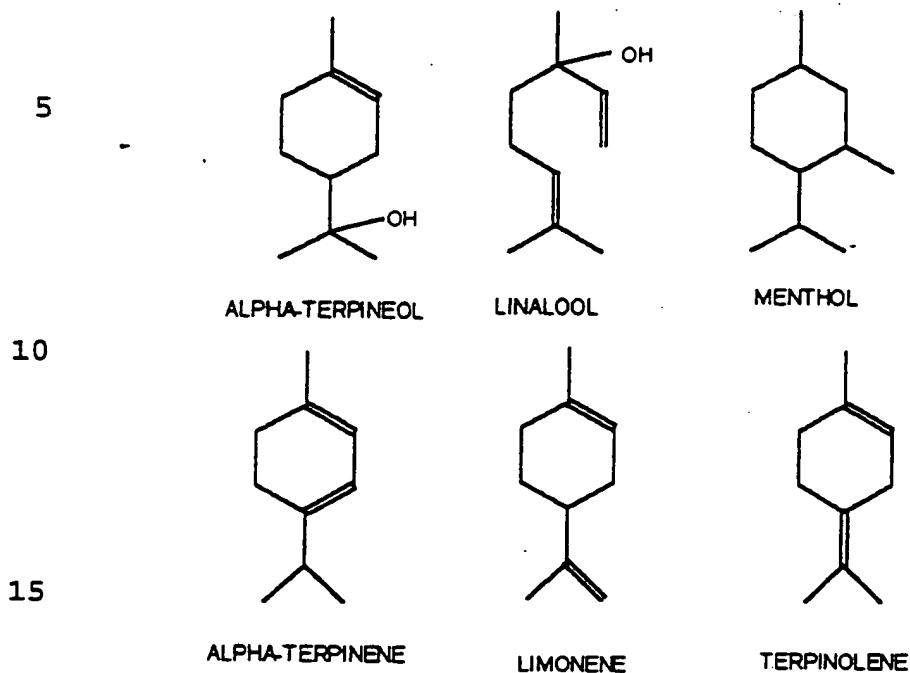


BETA-PINENE



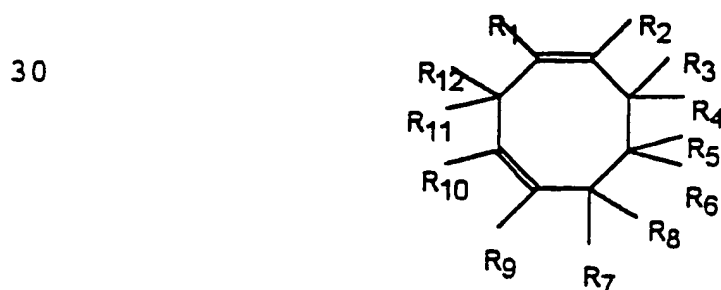
CAMPENE

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The organic cleaning solvent may also consist of linear, branched or cyclic hydrocarbons containing C<sub>10</sub> to C<sub>30</sub> species.

The organic cleaning fluid may also consist of hydrocarbon containing olefinic moieties which have been substituted with R<sub>1</sub>-R<sub>12</sub> groups, wherein R<sub>1</sub>-R<sub>12</sub> hydrogen atoms or alkyl groups containing 1-6 carbon atoms or both may comprise the substituted group, i.e.,

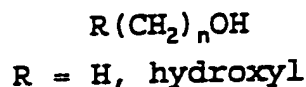


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This organic cleaning fluid may also be comprised of acyclic or cyclic monols or diols defined by the linear structure (1)

5

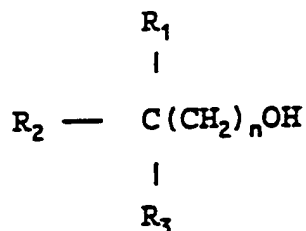
(1)



10 where n is selected from 1 to 20 or the branched structure (2)

(2)

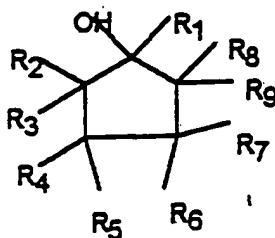
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20 where n is selected from 1 to 20 or the cyclic structure (3)

(3)

25

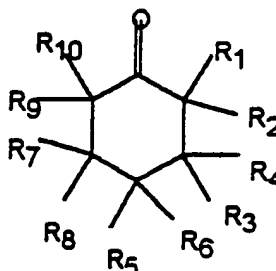


30 where  $R_1 - R_6$  is defined as alkyl or hydrogen groups of mixtures thereof, and n is defined as 0 to 6.

The organic fluid may also be comprised of linear, branched, or cyclic mono or polyketones, 35 such as

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5



where n is defined as 0 to 6 and  $R_1$ - $R_{10}$  is defined  
 10 as alkyl or hydrogen groups or mixtures thereof.

Other organic cleaning fluids applicable to  
 this invention may be comprised of:

(a) alkyl or aryl nitriles of the formula:

15

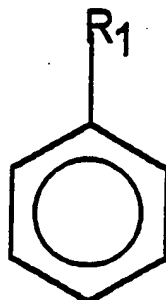


where R may be an alkyl group (methyl,  
 ethyl, etc), a phenyl group, or an alkyl  
 substituted phenyl group

20

(b) an alkylbenzene of the formula:

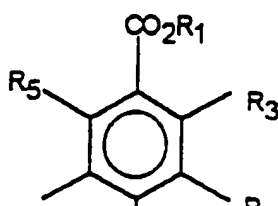
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(c) alkyl esters such as diethylphthalate  
 of the formula:

35





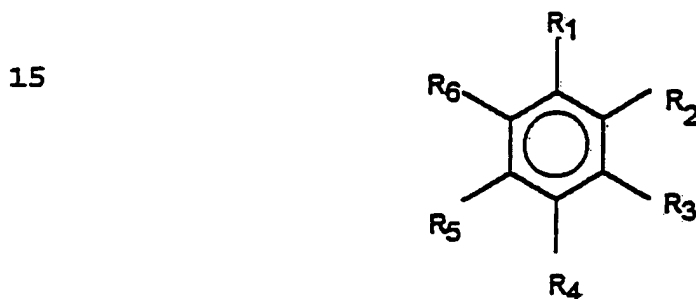
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(d) polyether alkanols of the formula:



where  $R_1$  is chosen from the class of compounds defined by H, alkyl, or hydroxyl groups and  $R_2$  is  
 10 selected from the class of compounds defined by H or alkyl or fluoroalkyl groups.

(e) substituted aromatics of the formula:



where  $R_1$ - $R_6$  is chosen from hydrogen, alkyl, fluoroalkyl, or halogen groups and combinations thereof, such as trifluorobenzene.

Such organic cleaning solvent may also  
 25 comprise mixtures of all the above organic cleaning solvents with fluorocarbons such as linear, branched, or cyclic perfluorocarbons or hydrofluorocarbons or hydrochlorofluorocarbons optionally with substituted oxygen, sulfur,  
 30 nitrogen, phosphorous or other halogen atoms attached to a carbon atoms and optionally with surfactant as a solubilizing agent.

The fluorocarbon rinse solvent may be selected from the class of hydrofluorocarbon or  
 35 hydrochlorofluorocarbon compounds or mixtures

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comprised of linear, branched, or cyclic structures having a boiling point of at least 25°C to 120°C and such fluorocarbons may be optionally substituted with other functional groups chosen from the class consisting of other halogens and oxygen, sulfur, nitrogen, and phosphorous atoms.

The hydrofluorocarbon preferred compounds or the hydrochlorofluorocarbon compounds have a certain miscibility for organic cleaning solvents in the boiling range of at least 25°C to 120°C so that at least 2 mole % of the hydrocarbon cleaning solvent is miscible with the fluorocarbon fluid without obtaining phase separation.

The hydrofluorocarbons preferably contain between 3 to 8 carbon atoms, hydrogen and fluorine in the compound. The boiling point is preferably between 25°C and 120°C with at least 60% of fluorine in the compound. The compounds preferably have a linear or branched chain.

Providing flammability suppression can be maintained through the use of suitable vapor blanketing species. The rinse solvent may also be selected from compounds or mixtures comprised of other linear, branched, or cyclic alkyl or aryl alcohols, esters, ethers, ketones, hydrocarbons, and other non-aqueous media.

Still other objects and advantages of the present invention will become readily apparent to

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those skilled in this art from the following detailed description, wherein only the preferred embodiments of the invention are shown and described, simply by way of illustration of the best mode contemplated of carrying out the invention. As will be realized, the invention is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, all without departing from the invention. Accordingly, the drawings and description are to be regarded as illustrative in nature, and not as restrictive.

#### Brief Description of Drawings

15

Figure 1 is a partial schematic view of degreasing or defluxing equipment that may be used in the multi-solvent non-aqueous cleaning system of the prevent invention;

20

Figure 2 is a schematic view depicting an alternative embodiment of equipment that may be used in the present invention;

Figure 3 is a schematic view depicting a further alternative embodiment of equipment for use in the present invention;

Figure 4 is a partial schematic view of yet further alternative equipment for practicing the system of the prevent invention;

Figure 5 it another embodiment of equipment for use in the present inventions and;

35 Figure 6 is a further embodiment of

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equipment for use in the present invention.

Best Mode for Carrying out the Invention

5        In its most basic form, the present invention is a novel non-aqueous cleaning process whereby the most attractive features of the semi-aqueous cleaning process and the solvent vapor degreasing solvent process are combined.

10       Specifically, a substrate or part to be cleaned (e.g., a printed circuit board coated with a rosin-based flux, or a metallic or nonmetallic part coated with a petroleum, synthetic, or semi-synthetic based oil or grease) is first washed in

15       a warm or ambient temperature hydrocarbon solvent tending to have a greater affinity for the soil or contaminant on the substrate than a fluorocarbon based solvent. The part is then rinsed by spray or immersion in a second tank or

20       cleaning region containing a nonflammable fluorocarbon solvent, preferably having a lower boiling point than the hydrocarbon solvent. The fluorocarbon solvent has at least slight volubility for the hydrocarbon solvent and

25       therefore rinses the hydrocarbon solvent from the surface of the part. The fluorocarbon solvent is then dried from the part surface by evaporation in a known manner. The benefit of this process is that drying costs are minimized, waste water

30       treatment costs and equipment and capital investments are virtually eliminated, and safety of operation is improved. Further, through the use of hydrofluorocarbon or perfluorocarbon solvents in the rinse and drying steps, the

35       environmental benefit is greatly improved over

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the chlorocarbon or chlorofluorocarbon solvent systems.

The organic cleaning agent is preferably a hydrocarbon which may be selected from linear or branched alkyl or alkanol monocarboxylic esters having at least six carbon atoms in the aliphatic moiety and at least one carbon atom in the ester moiety.

10

The organic hydrocarbon fluid may also be selected from linear or cyclic hydrocarbons containing at least one olefinic bond endo or exo to the ring.

15

The hydrocarbon may also be pinene and/or camphene.

The preferred hydrofluorocarbons are selected from the following groups:

(1) compounds with the empirical formula:

25  $C_3H_nF_8 - n$  where  $n \leq 4$

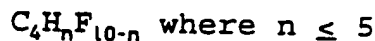
Representative examples of this class are:

30  $CH_2FCH_2FCHF_2$   
 $CH_2FCF_2CFH_2$   
 $CF_2HCH_2CF_2H$   
 $CF_2HCFHCF_2H$

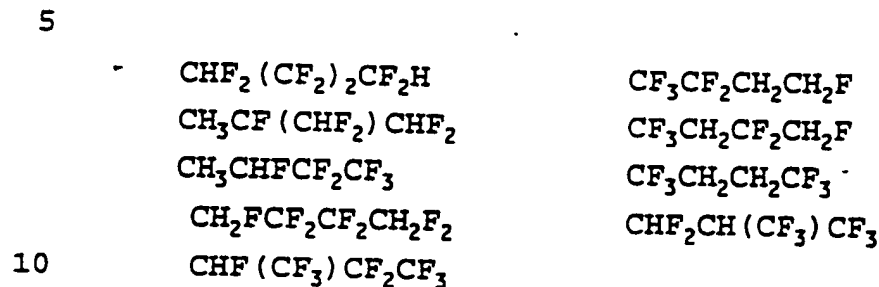
(2) linear or branched compounds of the empirical formula:

35

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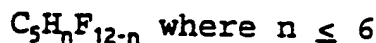


Representative examples of this class are:

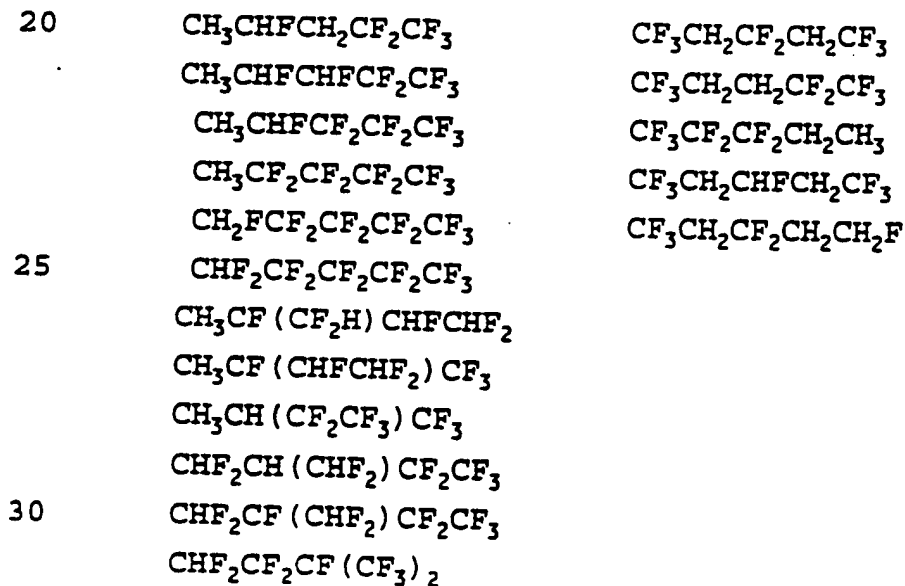


(3) linear or branched compounds of the empirical formula:

15



Representative examples of this class are:



(4) linear or branched compounds of the empirical formula:

35

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Representative examples of this class are:

- |    |  |   |
|----|--|---|
| 5  | CHF <sub>2</sub> (CF <sub>2</sub> ) <sub>4</sub> CF <sub>2</sub> H                                 | CF <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> |
|    | CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>    | (CF <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> CHCF <sub>3</sub>                               |
|    | CH <sub>3</sub> CH <sub>2</sub> CFHCFHCF <sub>2</sub> CF <sub>3</sub>                              |   |
|    | CH <sub>3</sub> CHFCH <sub>2</sub> CHFCH <sub>2</sub> CF <sub>3</sub>                              |   |
|    | CH <sub>3</sub> FCHFCH <sub>2</sub> CF <sub>2</sub> CHFCH <sub>2</sub> CF <sub>3</sub>             |   |
| 10 | CF <sub>2</sub> HCHFCH <sub>2</sub> CF <sub>2</sub> CHFCH <sub>2</sub> CF <sub>2</sub> H           |   |
|    | CH <sub>2</sub> FCF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> H |   |
|    | CHF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CHF <sub>2</sub>  |   |
|    | CHF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>   |   |
|    | CH <sub>3</sub> CH(CHFCH <sub>2</sub> CF <sub>3</sub> )CF <sub>3</sub>                             |   |
| 15 | CH <sub>3</sub> CF(CF <sub>2</sub> H)CHFCH <sub>2</sub> CF <sub>3</sub>                            |   |
|    | CH <sub>3</sub> CF(CF <sub>3</sub> )CHFCH <sub>2</sub> CF <sub>3</sub>                             |   |
|    | CH <sub>3</sub> CF <sub>2</sub> CF(CF <sub>3</sub> )CF <sub>2</sub> CH <sub>3</sub>                |   |
|    | CH <sub>3</sub> CF(CF <sub>3</sub> )CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>                |   |
|    | CHF <sub>2</sub> CF <sub>2</sub> CH(CF <sub>3</sub> )CF <sub>2</sub> CF <sub>3</sub>               |   |
| 20 | CHF <sub>2</sub> CF <sub>2</sub> CF(CF <sub>3</sub> )CF <sub>2</sub> CF <sub>3</sub>               |   |

(5) linear or branched compounds of the empirical formula:

25

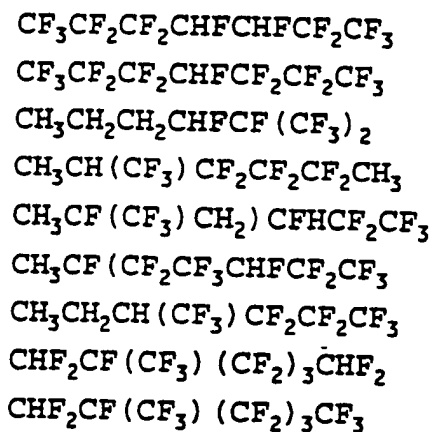


Representative examples of this class are:

- |    |  |
|----|--|
| 30 | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHFCH <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> |
|    | CH <sub>3</sub> CHFCH <sub>2</sub> CF <sub>2</sub> CHFCH <sub>2</sub> CF <sub>3</sub>              |
|    | CH <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>                                    |
|    | CH <sub>3</sub> CH <sub>2</sub> (CF <sub>2</sub> ) <sub>4</sub> CF <sub>3</sub>                    |
|    | CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>    |
| 35 | CH <sub>2</sub> FCF <sub>2</sub> CHF(CF <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>                |

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5

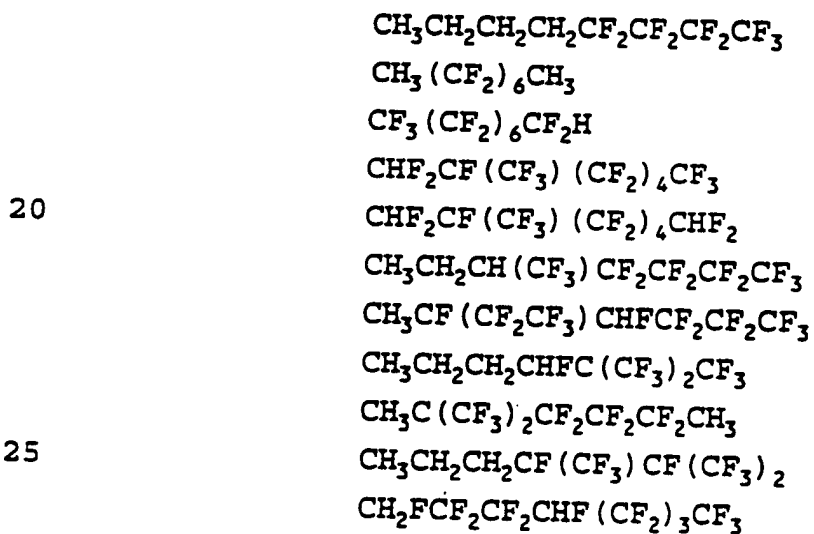


10

(6) Linear or branched compounds of the empirical formula  $\text{C}_8\text{H}_n\text{F}_{18-n}$  where  $n \leq 9$ .

Representative examples of this class are:

15



25

Figure 1 is a partial schematic illustration of one type of apparatus which can be used in the present process. Therein, a vessel 10 is divided into three sumps: a cleaning sump 15, a wash sump 20, and a rinsing sump 25. The cleaning compartment 15 is separated by one or more walls 17, 19 from the second compartment 20, which contains a fluorocarbon fluid 22 heated to its boiling point by a heater 34, to provide



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a nonflammable condensing vapor blanket 30 or a flammability suppression blanket over all the sumps 15, 20, 25 common to vessel 10. Compartment 20 also provides an area where the bulk of the soil and organic cleaning agent can be washed from the substrate by either immersing into the fluorocarbon fluid contained in compartment 20 or by placement in a spray stream 18 of pure fluorocarbon condensate, whereby the contaminated liquid drops into the sump below. The cleaning compartment 15 is adapted to contain a body of the organic cleaning solvent 24 tailored for the cleaning application, which could be an organic hydrocarbon as noted above and in the examples below for heavy duty cleaning, or a mixture of an organic hydrocarbon with a milder solvent such as a fluorocarbon for less rigorous cleaning applications (where compatibility with the substrate may be of more important consideration). The washing compartment 20 is adapted to contain a rinsing agent 22 having at least slight solubility for the cleaning solvent 24. As used throughout this specification, "slight solubility" of the rinsing fluorocarbon solvent for the hydrocarbon cleaning solvent is defined as  $\geq 2$  mole % of the hydrocarbon is soluble in fluorocarbon solvent. An appropriate rinsing agent 22 and one preferred in the present invention is a fluorocarbon based solvent as noted above and in the examples below. Optionally, a second rinsing compartment 25, which is at a cooler temperature than compartment 20, may be provided downstream from the first rinsing compartment, and is also adapted to contain the fluorocarbon solvent rinsing agent. The purpose of compartment 25 is to provide a final immersion rinse for the substrate to remove trace residues of soil or cleaning solvent and also to cool the substrate so that the part is rinsed

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with pure condensing vapor in the vapor zone 30. The vapor zone 30 is formed above the respective compartments 15, 20, 25 and a cooling coil 32 of a type known in the art (such as disclosed in U.S. Patent  
5 4,261,111 to Rand) defines the uppermost extent of the vapor zone 32 to condense vapor for return of condensate to compartment 25.

It is to be noted that the hydrocarbon cleaning  
10 solvent 24 and fluorocarbon rinsing fluid 22 may be chosen for their respective mutual solubilities such that some means of physical separation such as phase separation may be employed to remove built-up soils as well as to recycle clean organic solvent back to its  
15 originating sump. Therefore, with reference to Figure 1, it is to be noted that a U-tube phase separator (not shown) or weir or skimmer may be used in conjunction with compartment 20 to separate or remove condensed  
20 hydrocarbon which will float on top of the fluorocarbon, and this separation device (not shown) may be arranged so that the excess hydrocarbon fluid will flow back to the cleaning tank 15 from the rinsing tank 20.

The vessel 10 of Figure 1 is depicted as an open top  
25 type of defluxer or degreaser. However, it is to be understood that the vessel 10, in its schematic form, may also characterize an in-line type of degreaser or defluxer wherein conveyor means (not shown) may be used to successively convey the parts from the cleaning sump  
30 15 to the rinsing sumps 20 and 25.

In Figure 2, the organic cleaning fluid in cleaning tank 15 may optionally be mixed with a fluorocarbon type solvent. The cleaning fluid in this  
35 case would be warmed to a sufficient temperature to boil

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off the fluorocarbon, where the boiling point of the fluorocarbon should be at least 10°C. lower than that of the organic hydrocarbon fluid. The mixture is heated with coils 33 so that the resulting vapor zone immediately overlying the hydrocarbon is essentially a fluorocarbon-based nonflammable or flammability suppression vapor zone to minimize the possibility of explosion. The cleaning fluid mixture may or may not require a surfactant additive to ensure phase homogeneity between the organic hydrocarbon and the fluorocarbon solvents. The fluorocarbon which was boiled off would be maintained at a constant concentration in compartment 15 by either returning the vapor condensate back to this compartment and/or pumping fluid from the rinse compartment(s) 20,25 back to this sump through control with a volume or level sensingtransducer (not shown). In this variation of Figure 1, the boiling rinse sump 20 may not be necessary, or it could function purely as a second rinse sump at any intermediate temperature between compartment 15 and compartment 25. In the three-sump option where sump 20 supplies the fluorocarbon vapor to form the nonflammable blanket for vessel 10, sump 20 may be heated with heating coils 34 and heating coils 33 may not be necessary. In the two-sump option where sump 15 supplies the fluorocarbon vapor to form the nonflammable blanket 30 for vessel 10, heating coil 33 would be preferred and heating coil 34 may not be necessary. In the two-sump option where sump 15 supplies the fluorocarbon vapor to form the nonflammable blanket 30 for vessel 10, sump 20 may not be necessary and sump 25 would provide a cool liquid rinse immersion prior to bringing the cleaned substrate into the vapor condensing zone 30 for a final pure condensate rinse.

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In Figure 3, the rinse sump 20 may contain a saturated solution of the hydrocarbon based cleaning fluid and the fluorocarbon based rinsing solvent. The fluids are selected so that the hydrocarbon phase separates at some low concentration (i.e., less than 10 mole %) in the fluorocarbon and floats to the top of the more dense fluorocarbon, providing a cascading effect back into the cleaning sump 15. The rinse sump(s) 25a or 25b may also in turn cascade pure rinse solvent into sump 20 to maintain its level and also to directionally provide a flow skimming action to sweep the separated organic layer towards the boil sump 15.

In Figure 4, the boil sump 15 contains both hydrocarbon and fluorocarbon based solvents of sufficient immiscibility to form layered cleaning zones 5a and 15b. The advantage of this arrangement is that the heating coil 33, which provides the nonflammable vapor blanket for vessel 10, is now immersed in a fluorocarbon-rich phase which lessens the possibility of accidental fire if the liquid in the sump drops below its intended level. Furthermore, the boiling fluorocarbon liquid now provides an agitation action the top, less dense organic hydrocarbon phase to assist in the cleaning performance. As in Figure 3, the fluorocarbon rinse solvent and the hydrocarbon cleaning solvent can be cascaded or pumped back to their respective sumps to ensure that sump liquid volumes are maintained.

In Figure 5, the hydrocarbon cleaning zone 15 may be separated from the rinsing zones 20 and 25 by being provided within separate structures 11 and 12. This configuration is intended to provide the ability to retrofit conventional solvent vapor degreasing or defluxing batch-type equipment such as represented by

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vessel 12 in Figure 5 with the cleaning process of this invention. The carry-over of organic solvent from vessel 11 to vessel 12 can be reduced by mechanical devices such as an air knife 37. Nitrogen or any other nonflammable  
5 compressed gas may be introduced into the vapor zone overlying the hydrocarbon sump 15 to reduce hydrocarbon flammability or the danger of explosion, as typical with many types of conventional semi-aqueous (organic cleaning/aqueous rinse) cleaning processes. In the  
10 fluorocarbon boil sump 20, the residual hydrocarbon 20 carried over from cleaning sump 15 may be mechanically separated out as described in Figure 1 and recycled back with a pump 45 (as schematically depicted) in view of the physical separation of the two cleaning zones which would  
15 prevent cascading as in the previous embodiments.

In Figure 6, it is presumed that the organic cleaning solvent in cleaning sump 15 is immiscible or of low miscibility with the fluorocarbon-based rinsing solvent  
20 in rinsing sump 25. To prevent mixing of these solvents together and thereby potentially recontaminating the cleaned substrate, the first rinsing zone is provided with a coupling solvent (such as an alkanol like butanol, or another fluorochemical such as trifluorobenzene, or  
25 any other type of hydrocarbon) wherein the fluorocarbon solvent is miscible with the coupling solvent. Preferably, the fluorocarbon solvent has a lower boiling point than either the organic cleaning solvent or the coupling solvent. In this Case, the fluorocarbon in sump  
30 25 primarily serves the purpose of blanketing the flammable liquids in sumps 15 and 20 with a nonflammable vapor, and the level of liquid in rinse sump 20 which is comprised primarily of coupling solvent is maintained by makeup with fluorocarbon liquid from sump 25. The  
35 substrate which has been rinsed in coupling solvent sump

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20 is either subjected to a final immersion rinse in  
sumps(s) 25a and/or 25b or is held in the fluorocarbon  
condensing vapor zone 42 for a final rinse, which can be  
suitably accomplished since the coupling-solvent is  
5 miscible with the fluorocarbon solvent.

### EXAMPLES

The following examples are used to demonstrate the  
10 unexpected cleaning performance observed when a soiled  
coupon is first immersed in an organic cleaning solvent  
followed by a rinse with a fluorochemical solvent. In  
these studies, stainless steel coupons were coated with  
various commercial petroleum, semi-synthetic, and  
15 synthetic oils. The commercial petroleum oils are  
paraffinic, straight or branched chain saturated  
hydrocarbons. All of these oils are used in the metal  
working industry for cooling and lubricating purposes.  
The synthetic oils contain synthetic polymer with  
20 additives containing fatty acids and amines. The semi-  
synthetic oils are mixtures of the petroleum and  
synthetic oils. The cleaning process used for tests to  
demonstrate this invention consisted of 30 second  
immersion of a coupon in the organic cleaning solvent  
25 followed by a 30 second immersion in the fluorochemical  
solvent and a 30 second rinse above the liquid in the  
cooling coil zone with the condensing vapors of the  
fluorochemical solvent. The amount of soil on the coupon  
before and after cleaning was determined with a  
30 commercial CO<sub>2</sub> coulometer, which measures to microgram  
sensitivity the amount of organic residue, expressed in  
carbon units, on a surface. The sample of residue on the  
coupon is introduced into a combustion furnace via a  
sample boat, and is combusted in oxygen atmosphere at a  
35 temperature of 650°C. The resulting CO<sub>2</sub> and other

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oils, using an organic cleaning step followed by a fluorochemical vapor rinse step resulted in completely cleaning the coupon surface (>99.9% removal of carbon). However, in experiments (b) and (e), significant amount of carbon remained on the surface when the coupon was cleaned by a 30 second immersion in basic ester only followed by a 30 second drying in air without the HFC vapor rinse. In experiments (c) and (f), significant amount of carbon residue remained on the surface when the coupon was cleaned by a second immersion in HFC-365 followed by a 30 second drying in air without using the ester cleaning step. This example demonstrates that a fluorochemical vapor rinse step is required to completely clean a soiled surface which has been immersed in either a dibasic ester or a mixture of a dibasic ester with fluorochemical, and neither the ester alone nor the fluorochemical solvent alone is sufficient to completely clean the surface.

20

Example Three

Soiled coupons were immersed in a 50/50 volume % mixture of cyclohexanone, a cyclic ketone, and HFC-365, a hydrofluorocarbon, for 30 seconds at 57-59°C followed by a 30 second immersion in HFC-365 at ambient temperature and a 30 second vapor rinse with HFC-365. The following results were noted:

30

Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(a)	petroleum	this invention	819	8.7

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Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(b)	petroleum	no HFC rinse	819	1064
(c)	petroleum	no ketone cleaning	819	70
(d)	synthetic	this invention	508	3.7
(e)	synthetic	no HFC rinse	508	1475
(f)	synthetic	no ketone cleaning	508	499
(g)	mineral oil	this invention	950	7.5
(h)	synthetic	this invention	1033	14.9

In experiments (a) through (f) using an organic cleaning step followed by a fluorochemical vapor rinse step resulted in completely cleaning the coupon surface (>99.9% removal of carbon). However, in experiments (b) and (e), a significant amount of carbon remained on the surface when the coupon was cleaned by a 30 second immersion in cyclohexanone only followed by a 30 second drying in air without the HFC vapor rinse. In experiments (c) and (f), a significant amount of carbon residue remained on the surface when the coupon was cleaned by a 30 second immersion in HFC-365 followed by a 30 second drying in air without using the ketone cleaning step. This example demonstrates that a fluorochemical vapor rinse step is required to completely clean a soiled surface which has been immersed in either a ketone (cyclic or a cyclic) with fluorochemical, and neither the ketone alone nor the fluorochemical solvent alone is



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sufficient to completely clean the surface.

Example Four

5 Soiled coupons were immersed in a 50/50 volume % mixture of liquid cyclohexanol, a cyclic alkanol, and HFC-365, a hydrofluorocarbon, for 30 seconds at 57-59°C followed by a 30 second immersion in HFC-365 at ambient temperature and a 30 second vapor rinse with HFC-365. The  
10 following results were noted:

Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(a)	petroleum	this invention	819	4
15 (b)	petroleum	no HFC rinse	819	2397
(c)	petroleum	no alkanol cleaning	819	70
(d)	synthetic	this invention	508	139.7
(e)	synthetic	no HFC rinse	508	1148
(f)	synthetic	no alkanol cleaning	508	499
20 (g)	mineral oil	this invention	950	12.7
(h)	synthetic	this invention	1033	10.2

In the experiments with petroleum oil, using an  
25 organic cleaning step followed by a fluorochemical

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vapor rinse step resulted in completely cleaning the coupon surface (>99.9% removal of carbon). Since cyclohexanol is a fairly poor solvent in cleaning synthetic oil, as shown in experiments (b) and (e), most of the oil and the organic solvent film was able to be removed with the cleaning process of this invention as shown in experiment (d). Additionally, in experiments (b) and (e), a significant amount of carbon remained on the surface when the coupon was cleaned by a 30 second immersion in cyclohexanol only followed by a 30 second drying in air without the HFC vapor rinse. In experiments (c) and (f), significant amount of carbon residue remained on the surface when the coupon was cleaned by a 30 second immersion in HFC-365 followed by a 30 second drying in air without using the alkanol cleaning step. This example demonstrates that a fluorochemical vapor rinse step is required to completely clean a soiled surface which has been immersed in an alkanol (cyclic or a cyclic), and neither the alkanol alone nor the fluorochemical solvent alone is sufficient to completely clean the surface.

#### Example Five

Soiled coupons were immersed in a 50/50 volume % mixture of liquid 1, 5-dimethylcyclooctadiene, a cyclic olefin, and HFC-365, a hydrofluorocarbon, for 30 seconds at 57-59°C followed by a 30 second immersion in HFC-365 at ambient temperature and a 30 second vapor rinse with HFC-365. The following results were noted:

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Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(a)	petroleum	this invention	819	10.1
(b)	petroleum	no HFC rinse	819	2953
5 (c)	petroleum	no olefin cleaning	819	70
(d)	synthetic	this invention	508	18.8
(e)	synthetic	no HFC rinse	508	2831
(f)	synthetic	no olefin cleaning	508	499
(g)	mineral oil	this invention	950	10
10 (h)	synthetic	this invention	1033	15.1

In the experiments with petroleum oil and synthetic oil, using an organic cleaning step followed by a fluorochemical vapor rinse step resulted in completely cleaning the coupon surface (>99.8% removal of carbon). However, in experiments (b) and (e), significant amount of carbon remained on the surface when the coupon was cleaned by a 30 second immersion in 1,5-dimethylcyclooctadiene only followed by a 30 second drying in air without the HFC vapor rinse. In experiments (c) and (f), significant amount of carbon residue remained on the surface when the coupon was cleaned by a 30 second immersion in HFC-365 followed by a 30 second drying in air without using the olefin solvent cleaning step. This example demonstrates that a fluorochemical vapor rinse step is required to completely clean a soiled

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surface which has been immersed in an olefin (cyclic or acyclic), and neither the olefin alone nor the fluorochemical solvent alone is sufficient to completely clean the surface.

5

Example Six

Soiled coupons were immersed in a 50/50 volume % mixture of liquid benzotrifluoride, a fluorinated aromatic chemical, and HFC-365, a hydrofluorocarbon, for 10 30 seconds at 57-59°C followed by a 30 second immersion in HFC-365 at ambient temperature and a 30 second vapor rinse with HFC-365. The following results were noted:

15

20

Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(a)	petroleum	this invention	819	13.3
(b)	petroleum	no HFC rinse	819	138
(c)	petroleum	no fl. org. cleaning	819	70
(d)	synthetic	this invention	508	16.1
(e)	synthetic	no HFC rinse	508	1022
(f)	synthetic	no fl. org. cleaning	508	499
(g)	mineral oil	this invention	950	13.7
(h)	synthetic	this invention	1033	127.9

25

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In the experiments with petroleum oil and synthetic oil, using an organic cleaning step followed by a fluorochemical vapor rinse step resulted in completely cleaning the coupon surface (>99.8% removal of carbon).  
5 However, in experiments (b) and (e), significant amount of carbon remained on the surface when the coupon was cleaned by a 30 second immersion in benzotrifluoride only followed by a second drying in air without the HFC vapor rinse. In experiments (c) and (f), significant amount of  
10 carbon residue remained on the surface when the coupon was cleaned by a 30 second immersion in HFC-365 followed by a 30 second drying in air without using the fluoroaromatic cleaning step. This example demonstrates that a fluorochemical vapor rinse step is required to  
15 completely clean a soiled surface which has been immersed in a fluorinated aromatic solvent, and neither the fluoroaromatic cleaning solvent alone nor the fluorochemical solvent alone is sufficient to completely clean the surface.

20

Example Seven

Soiled coupons were immersed in a 50 volume % mixture of polyethylene glycol (MW 200), a polyether diol, a  
25 methyl ester, and 50 volume % of HFC-365, a hydrofluorocarbon, for 30 seconds at 45-50°C followed by a 30 second immersion in HFC-365 at ambient temperature and a 30 second vapor rinse with HFC-365. The following results were noted:

30

35

-35-

Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(a)	petroleum	this invention	819	14
(b)	petroleum	no HFC rinse	819	1917
(c)	petroleum	no PEG/ester cleaning	819	70
(d)	synthetic	this invention	508	11
(e)	synthetic	no HFC rinse	508	1847
(f)	synthetic	no PEG/ester cleaning	508	499
(g)	mineral oil	this invention	950	12
(h)	synthetic	this invention	1033	13

In the experiments with petroleum oil and synthetic oil, using an organic cleaning step followed by a fluorochemical vapor rinse step resulted in completely cleaning the coupon surface (>99.8% removal of carbon). However, in experiments (b) and (e), significant amount of carbon remained on the surface when the coupon was cleaned by a 30 second immersion in polyethylene glycol/methyl ester solvent mixture only followed by a 30 second drying in air without the HFC vapor rinse. In experiments (c) and (f), significant amount of carbon residue remained on the surface when the coupon was cleaned by a 30 second immersion in HFC-365 followed by a 30 second drying in air without using the

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glycol/ester solvent cleaning step. This example demonstrates that a fluorochemical vapor rinse step is required to completely clean a soiled surface which has been immersed in a mixture of glycol with an ester, and  
5 neither the mixed organic solvent alone nor the fluorochemical solvent alone is sufficient to completely clean the surface.

#### Example Eight

10

Soiled coupons were immersed in either a methyl ester, or a mixture of polyethylene glycol (MW 200), a polyether diol, and a methyl ester, for 30 seconds at 57-59°C followed by a 30 second immersion in either HCFC-  
15 123, a hydrochlorofluorocarbon, or HFC-52-13, a highly fluorinated alkane, at ambient temperature and a 30 second vapor rinse with either fluorochemical solvent. The following results were noted:

20

(a) The synthetic oil and the grease Valvoline were both removed from metal coupons to better than 99.9% using the PEG-200/methyl ester cleaning solvent mixture with HCFC-123 as the rinse solvent in the process of this invention.

25

(b) The synthetic oil and the grease Valvoline were both removed from metal coupons to better than 99.9% using the PEG-200/methyl ester cleaning solvent mixture with HFC 52-13 as the rinse solvent in the process of  
30 this invention.

#### Example Nine

Soiled coupons were immersed in a 50/50 volume %  
35 mixture of BIOACT EC-7, a commercial blend of terpenes

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and non-ionic surfactants, and HFC-365, a hydrofluorocarbon, for 30 seconds at 57-59°C followed by a 30 second immersion in HFC-365 at ambient temperature and a 30 second vapor rinse with HFC-365. The following results were noted:

Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(a)	petroleum	this invention	819	15.3
(b)	petroleum	no HFC rinse	819	2221
(c)	petroleum	no terpene cleaning	819	36
(d)	synthetic	this invention	508	13.6
(e)	synthetic	no HFC rinse	508	2272
(f)	synthetic	no terpene cleaning	508	27.9
(g)	mineral oil	this invention	950	12
(h)	mineral oil	no terpene cleaning	950	94
(i)	synthetic	this invention	1033	13
(j)	synthetic	no terpene cleaning	1033	340

In the experiments with petroleum oil and synthetic oil, using an organic cleaning step followed by a fluorochemical vapor rinse step resulted in virtually complete cleaning of the coupon surface (>99.6% removal of carbon). However, in experiments (b) and (e), significant amount of carbon remained on the



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surface when the coupon was cleaned by a 30 second immersion in the terpene solvent mixture only followed by a 30 second drying in air without the HFC vapor rinse. In experiments (c) and (f), significant amount of carbon residue remained on the surface when the coupon was cleaned by a 30 second immersion in HFC-365 followed by a 30 second drying in air without using the terpene solvent cleaning step. This example demonstrates that a fluorochemical vapor rinse step is required to completely clean a soiled surface which has been immersed in a terpene solvent, and neither the terpene solvent alone nor the fluorochemical solvent alone is sufficient to completely clean the surface.

15

#### Example Ten

Soiled coupons were immersed in 50/50 volume % mixture of liquid cyclohexanone, a cyclic ketone, and HFC-365, a hydrofluorocarbon, for 30 seconds at 56-59°C followed by a 30 second immersion in a nonflammable constant-boiling blend of 5% HCFC-141b, a hydrochlorofluorocarbon, and 90% HFC-365, a hydrofluorocarbon, at ambient temperature and a 30 second vapor rinse with the condensing azeotropic vapors of HCFC141b/HFC-365. The following results were noted:

30

35

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Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(a)	petroleum	this invention	819	18
(b)	petroleum	no HFC/HCFC blend rinse	819	2221
(c)	petroleum	no ketone cleaning	819	70
(d)	synthetic	this invention	508	29
(e)	synthetic	no HFC/HCFC blend rinse	508	2272
(f)	synthetic	no ketone cleaning	508	499
(g)	mineral oil	this invention	950	15
(h)	synthetic	this invention	1033	25

In the experiments with petroleum oil and synthetic oil, using an organic cleaning step followed by a fluorochemical blend of HCFC and HFC vapor rinse step resulted in virtually complete cleaning of the coupon surface (>99.8% removal of carbon). However, in experiments (b) and (e), significant amount of carbon remained on the surface when the coupon was cleaned by a 30 second immersion in the ketone cleaning solvent only followed by a 30 second drying in air without the HCFC/HFC vapor rinse. In experiments (c), (f), (h) and (j), more carbon residue remained on the surface when the coupon was cleaned by a 30 second immersion in HCFC-

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141b/HFC-365 azeotrope followed by a 30 second drying in air than in the dual solvent process of this invention using the terpene solvent cleaning step. This example demonstrates that even when a strong fluorochemical rinse solvent such as a blend containing HFCF-141b is used, the combined organic (ketone) cleaning step followed by a fluorochemical rinse step produces greater cleaning than if a ketone solvent alone or a fluorochemical solvent alone is used to clean the substrate.

10

Example Eleven

Soiled coupons were immersed in a 50/50 volume % mixture of liquid cyclohexanone, a cyclic ketone, and HFC-365/FC-72 (95:5 by weight) for 30 seconds at 56-59°C followed by a 30 second immersion in a non segregating blend of 5% FC-72, a perfluorocarbon, and 95% HFC-365, a hydrofluorocarbon, at ambient temperature and a 30 second vapor rinse with the condensing azeotropic vapors of FC-72/HFC-365. the following results were noted:

20

Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(a)	petroleum	this invention	819	22
(b)	petroleum	no ketone cleaning	819	44.3
(c)	synthetic	this invention	508	20.1
(d)	synthetic	no ketone cleaning	508	453

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Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(e)	mineral oil	this invention	950	21.3
(f)	mineral oil	no ketone cleaning	950	550
(g)	synthetic	this invention	1033	20.4
(h)	synthetic	no ketone cleaning	1033	426

In the above experiments, using an organic cleaning step followed by a fluorochemical vapor rinse step resulted in complete cleaning of the coupon surface (99.9% removal of carbon). More carbon residue remained on the surface when the coupon was cleaned by a 30 second immersion in the mixture of FC-72/HFC-365 followed by a 30 second drying in air without using the cyclohexanone solvent cleaning step. This example demonstrates that a fluorochemical vapor rinse step is required to completely clean a soiled surface which has been immersed in a ketone solvent, and neither the ketone solvent alone nor the fluorochemical solvent alone is sufficient to completely clean the surface. In addition, it is well known that perfluorocarbons such as FC-72 are very poor solvents for oils, but when blended with hydrochlorocarbons or even hydrochlorofluorocarbons in the vapor or immersion rinse step of this process combined with an organic cleaning step, the dual solvent process produces completely clean coupons which could not be completely cleaned by the individual solvent themselves.

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Example Twelve

Soiled coupons were immersed in liquid cyclohexanol, a cyclic alcohol, which was not admixed with the HFC prior to cleaning (as in the previous examples). The coupons were immersed for 30 seconds at 56-59°C followed by a 30 second immersion in HFC-365, a hydrofluorocarbon, at ambient temperature and a 30 second vapor rinse with the condensing azeotropic vapors of HFC-365. The following results were noted:

Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(a)	petroleum	this invention	819	18.5
(b)	synthetic	this invention	508	166
(c)	mineral oil	this invention	950	20.9
(d)	synthetic	this invention	1033	22.4

In this experiment, the cleaning ability of the organic cleaner segregated from the HFC was demonstrated. The results are within experimental error to those of Example 4, where the admixed organic/solvent system was evaluated. Interestingly, in this example the HFC/organic mixture in the cleaning sump cleaned better than if the cleaning sump contained only organic solvent (cyclohexanol).

Example Thirteen

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Soiled coupons were immersed in liquid cyclohexanone, a cyclic ketone, which was not admixed with the HFC prior to cleaning (as in the previous examples). The coupons were immersed for 30 seconds at 56-59°C followed by a 30 second immersion in HFC-365, a hydrofluorocarbon, at ambient temperature and a 30 second vapor rinse with the condensing azeotropic vapors of HFC-365. The following results were noted:

Expt.	Oil on Substrate	Cleaning Method	Micrograms (ug) Carbon on the Surface	
			Before Cleaning	After Cleaning
(a)	petroleum	this invention	819	11.3
(b)	synthetic	this invention	508	12.2
(c)	mineral oil	this invention	950	11.7
(d)	synthetic	this invention	1033	10.3

In this experiment, the cleaning ability of the organic cleaner segregated from the HFC was demonstrated. The results are within experimental error to those of Example 12, where the admixed organic/solvent system was evaluated. It will be readily seen by one of ordinary skill in the art that the present invention fulfills all of the objects set forth above. After reading the foregoing specification, one of ordinary skill will be able to effect various changes, substitutions of equivalents and various other aspects of the invention as broadly disclosed herein. It is therefore intended that the protection granted hereon be limited only by the definition contained in the appended claims and equivalents thereof.

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CLAIMS

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1. A non-aqueous cleaning process for removing residual soils or surface contamination from a part, comprising the steps of:

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(a) introducing the part into an organic cleaning fluid of sufficient solvency to substantially remove the contamination from said part;

15

(b) removing said part from said organic cleaning fluid and rinsing said part with a rinsing agent of lesser solvency for said soils or surface contamination but with at least slight solubility for said organic cleaning agent to remove said organic cleaning agent from said part, said rinsing agent selected from the class of hydrofluorocarbon compounds or mixtures containing between 3 and 8 carbon atoms with at least 60% of fluorine in the compound, said compounds having linear or branched chains with a boiling point between about 25° to about 125°C; and

25

(c) drying said part.

2. The process of claim 1, wherein the organic cleaning fluid is disposed in a cleaning compartment and the hydrofluorocarbon rinsing fluid is disposed in a rinse compartment.

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3. The process of claim 2, comprising the further step of heating the HFC rinsing fluid to form a flammability suppression blanket over the cleaning and rinsing compartments.

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4. The process of claim 3, comprising the further step of providing a final immersion rinse of said parts in a second rinse compartment containing HFC rinsing fluid to remove trace residues of soil or hydrocarbon cleaning fluid and to cool the part so that the part is  
5 rinsed in pure condensing vapor.

5. The process of claim 3, further comprising the step of phase separating any hydrocarbon cleaning fluid  
10 from the fluorocarbon rinsing fluid and recycling the separated clean hydrocarbon cleaning fluid back to the cleaning sump.

6. A non-aqueous cleaning process for removing  
15 residual soils or surface contamination from a part, comprising the steps of:

(a) introducing the part into a cleaning compartment containing a hydrocarbon cleaning solvent  
20 mixed with a hydrofluorocarbon solvent which resulting mixture substantially removes contamination from said part and wherein the mixture is heated to a sufficient temperature to boil off at least some of the hydrofluorocarbon having a boiling point less than the  
25 hydrocarbon fluid so that the resulting vapor zone overlying the cleaning fluid is essentially a fluorocarbon based flammability suppression vapor zone; and

30 (b) drying said part.

7. The process of claim 1 or 6, wherein said hydrofluorocarbons are selected from the following groups:

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(1) compounds with the empirical formula:



(2) linear or branched compounds of the empirical  
5 formula;



(3) linear or branched compounds of the empirical  
10 formula:



(4) linear or branched compounds of the empirical  
15 formula:



(5) linear or branched compounds of the empirical  
20 formula:



(6) linear or branched compounds of the empirical  
25 formula:



8. The process of claim 7, wherein the  
hydrocarbon is selected from linear or branched alkyl  
or alkenyl monocarboxylic esters having at least six  
carbon atoms in the aliphatic moiety and at least one  
30 carbon atom in the ester moiety.

9. The process of claim 7, comprising the further  
step of mixing a surfactant additive into the cleaning  
fluid mixture to insure phase homogeneity between the  
35 hydrocarbon and the hydrofluorocarbon solvents.

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10. The process of claim 8, comprising the further step of rinsing the parts to remove said blend therefrom from exposing said parts to substantially only HFC solvent in a rinsing compartment.

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11. The process of claim 10, comprising the further step of maintaining the concentration of HFC solvent in the blend at a substantially constant concentration by at least one of returning HFC solvent vapor condensate from a vapor zone above the blend back into the cleaning compartment containing the blend or pumping HFC solvent from the rinse compartment back to the cleaning compartment.

12. The process of claim 1, wherein said cleaning compartment containing the hydrocarbon cleaning fluid also contains HFC solvent of sufficient immiscibility with the hydrocarbon cleaning fluid to form layered cleaning zones within the cleaning compartment with the HFC rich phase forming the lower layer, and comprising the further step of heating said lower layer with a heating coil disposed therein to provide a flammability suppression vapor blanket above the cleaning compartment and whereby the resulting boiling HFC solvent provides an agitation action to the top layer, less dense hydrocarbon cleaning fluid to assist in the cleaning performance.

13. The process of claim 1 or 12, wherein said HFC solvent and said hydrocarbon cleaning fluid are selected so that any hydrocarbon fluid present in the rinsing compartment containing the HFC rinsing solvent separates at a predetermined low concentration from the HFC solvent and floats to the top of it to provide a cascading effect of hydrocarbon cleaning fluid back

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into the cleaning compartment.

14. The process of claim 13, comprising the step of providing a second rinsing compartment containing  
5 substantially entirely only HFC solvent and providing a cascading effect of pure HFC rinse solvent into the first rinsing compartment to maintain a predetermined level thereof and to directionally provide a flow  
skimming action to sweep the separated hydrocarbon  
10 cleaning fluid back toward the cleaning compartment.

15. The process of claim 1, comprising the further step of housing the hydrocarbon cleaning zone in a structure which is separate from a structure  
15 containing the rinsing zone.

16. The process of claim 15, comprising the further step of preventing the carryover of hydrocarbon cleaning fluid from the cleaning structure to the  
20 rinsing structure by the interpositioning of an air knife between the two said structures.

17. The process of claim 15, comprising the further step of introducing into the vapor zone  
25 overlying the hydrocarbon cleaning fluid a non-flammable gas to reduce hydrocarbon flammability and the danger of explosion.

18. The process of claim 15, comprising the  
30 further step of mechanically separating residual hydrocarbon cleaning fluid carried from the cleaning compartment to the rinsing compartment and recycling by pumping said hydrocarbon back into the cleaning compartment.

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19. The process of claim 1, wherein the hydrocarbon cleaning fluid and the HFC rinsing solvent are generally immiscible, and comprising the further step of providing between the hydrocarbon cleaning zone and the HFC rinsing zone, an initial rinsing zone containing a coupling solvent which is miscible with the HFC solvent.

20. A cleaning composition for removing residual soils or surface contamination from a part, said composition comprising a hydrocarbon compound and a hydrofluorocarbon compound containing at least 60% of fluorine in the compound, and linear or branched chain structures having between 3 and 7 carbon atoms.

21. The composition of claim 20, wherein said hydrofluorocarbons are selected from the following groups:

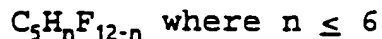
(1) compounds with the empirical formula:



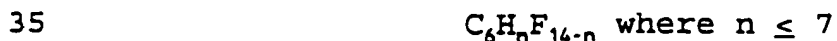
(2) linear or branched compounds of the empirical formula:



(3) linear or branched compounds of the empirical formula:



(4) linear or branched compounds of the empirical formula:



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(5) linear or branched compounds of the empirical formula:



5 (6) linear or branched compounds of the empirical formula:



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FIG. 1

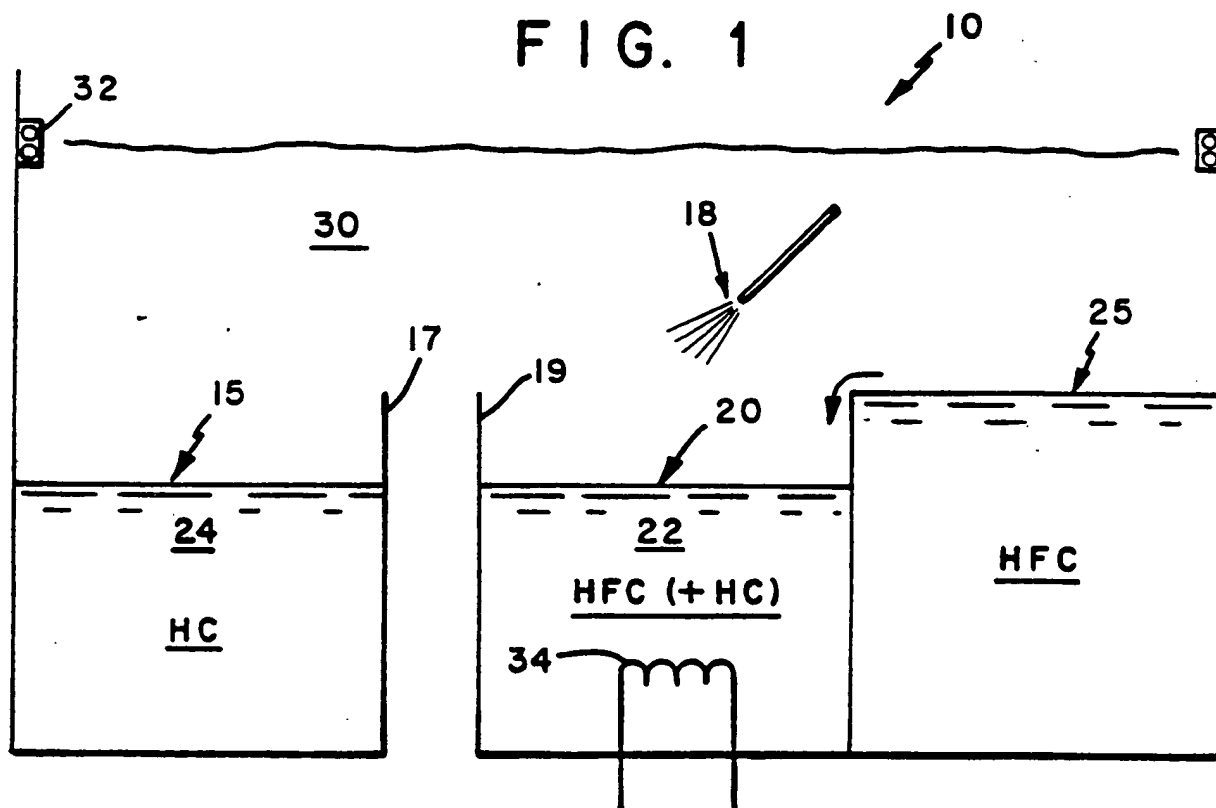
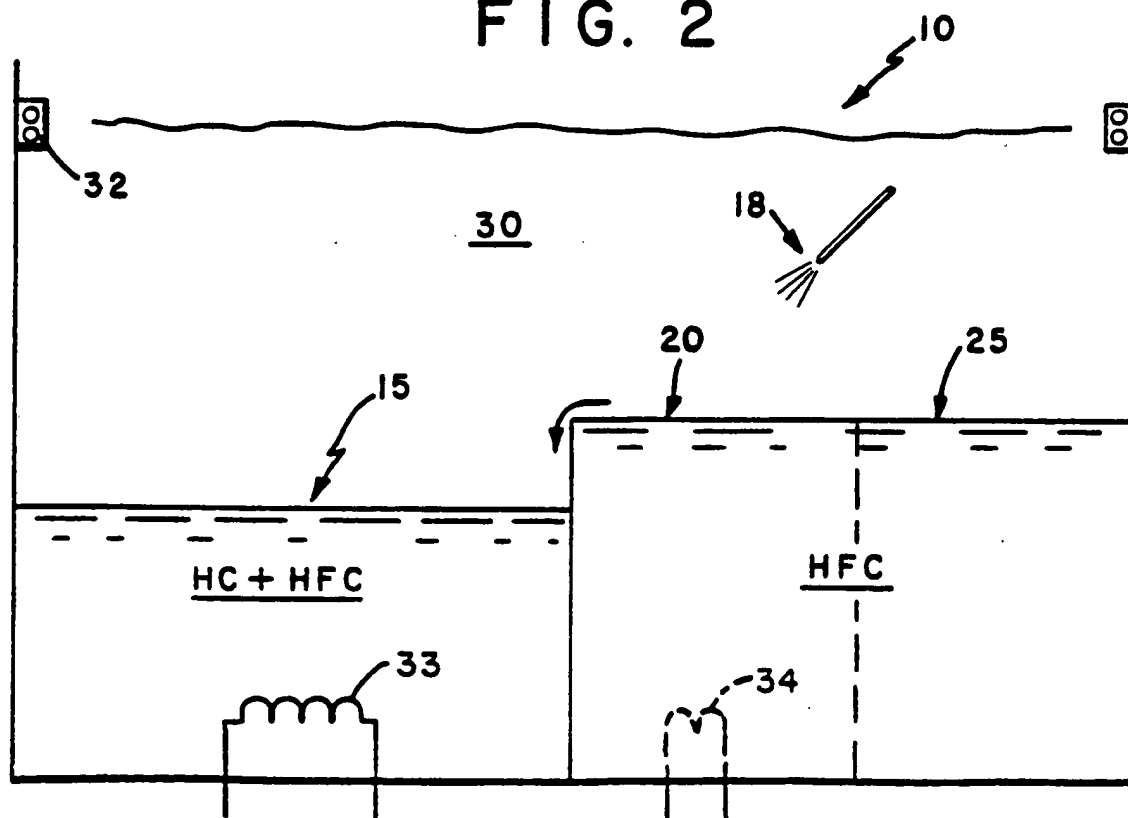


FIG. 2



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FIG. 3

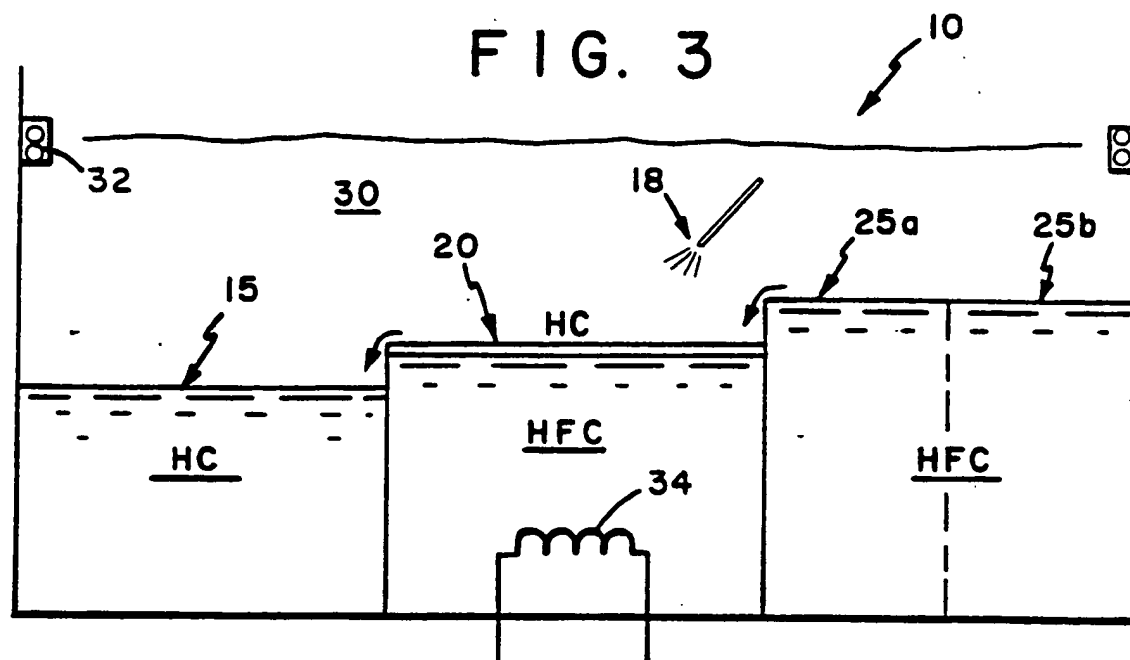
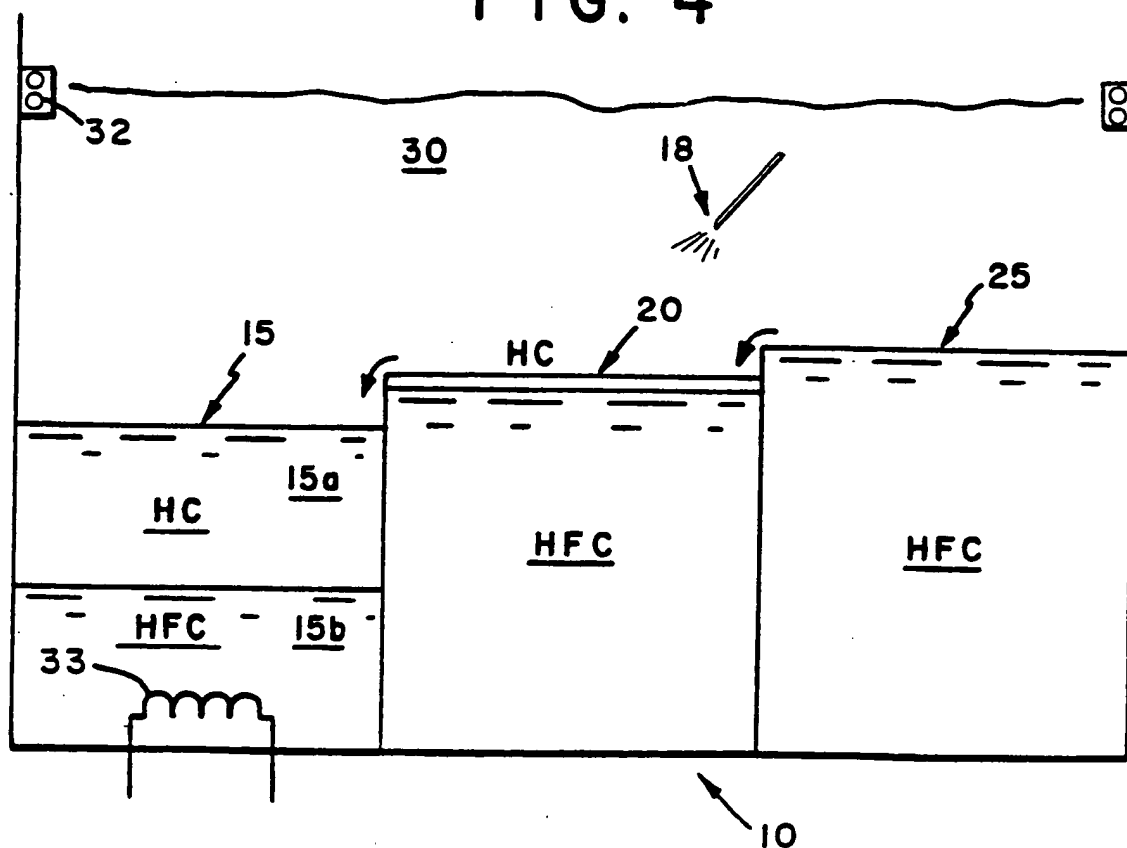


FIG. 4



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FIG. 5

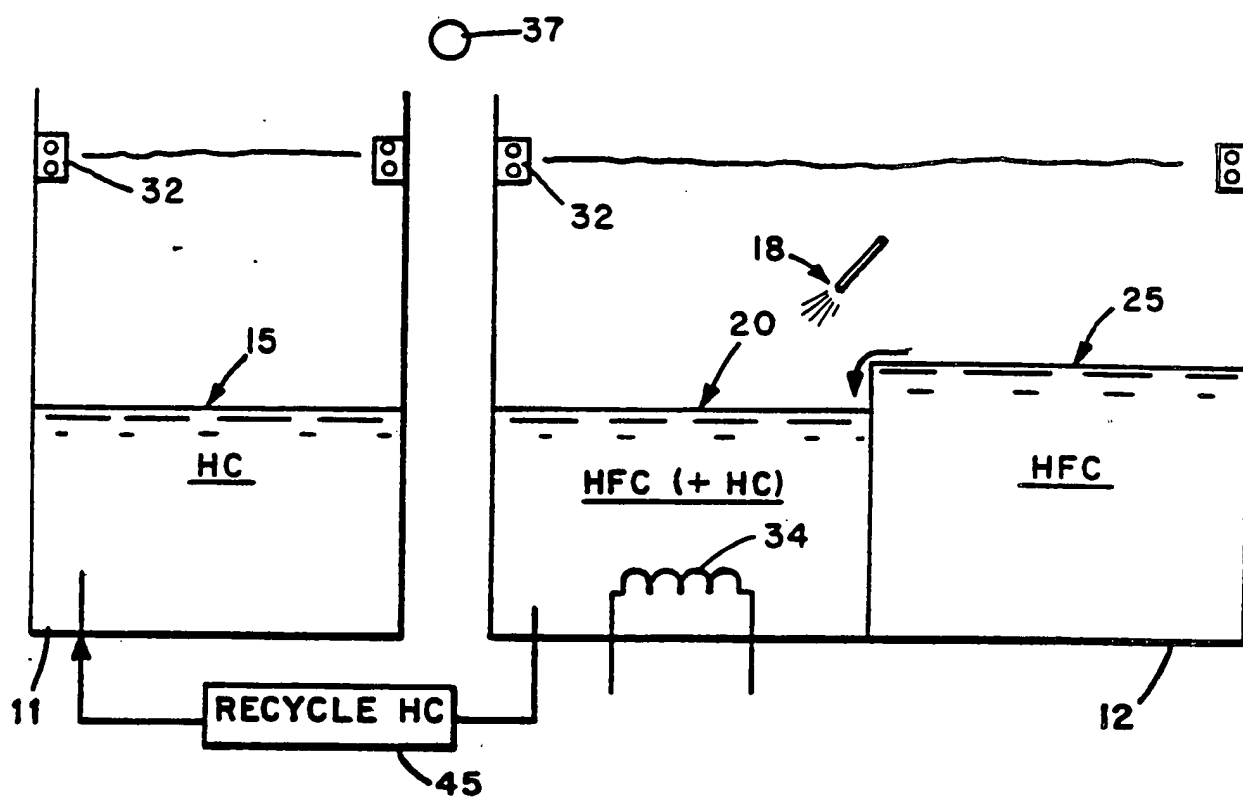
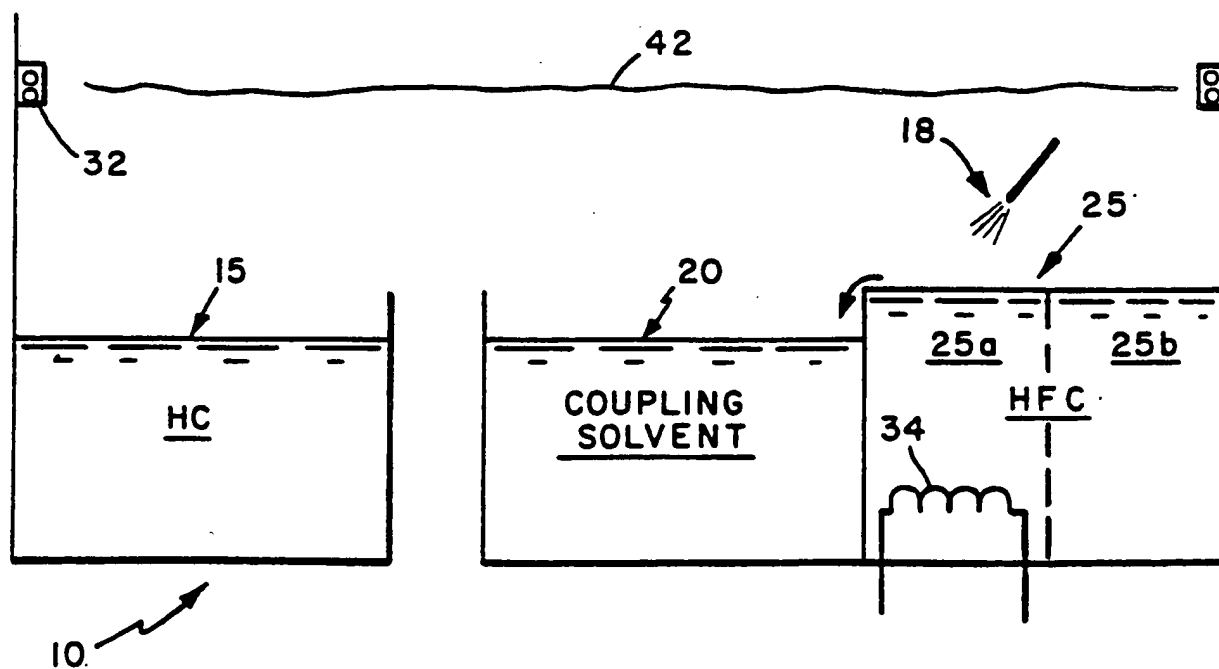


FIG. 6





## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/10291

**I. CLASSIFICATION OF SUBJECT MATTER** (If several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C23G5/02; C23G5/04

**II. FIELDS SEARCHED**Minimum Documentation Searched<sup>7</sup>

Classification System	Classification Symbols
Int.Cl. 5	C23G

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>**III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>**

Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP,A,0 350 316 (ISC CHEMICALS LIMITED) 10 January 1990	1,6,7, 12,15,16
Y	see page 3, line 33 - line 56; claims 1-12; figures 1,2; table 2 ---	2-5,13, 14,18
X	EP,A,0 431 458 (DAIKIN INDUSTRIES, LIMITED) 12 June 1991 see claims 1-6; examples 1-4 ---	20,21
Y	FR,A,2 198 795 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) 5 April 1974 see claims 1-36 ---	2-5,13, 14,18
A	WO,A,9 109 105 (E.I. DU PONT DE NEMOURS AND COMPANY) 27 June 1991 see claims 1,2 ---	6-9
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<sup>9</sup> Special categories of cited documents: <sup>10</sup>

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

<sup>11</sup> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<sup>12</sup> document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<sup>13</sup> document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<sup>14</sup> document member of the same patent family**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

26 MARCH 1993

Date of Mailing of this International Search Report

22.04.93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

LANDAIS A.M.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category <sup>a</sup>	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9210291  
SA 67940

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on  
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